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(54) **Treating subterranean formations**

(57) A subterranean formation is treated with a high viscosity treating fluid comprising water, a hydrated galactomannan gelling agent and a borate crosslinking

composition basically comprised of a low viscosity hydrocarbon liquid, an organophilic clay, a slightly water soluble borate, a buffer and a dispersing agent.

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Description

[0001] The present invention relates to a method of treating a subterranean well using a borate cross-linking composition

[0002] High viscosity aqueous cross-linked gels are used in a variety of operations and treatments carried out in oil and gas wells. Such operations and treatments include, but are not limited to, well completion operations, fluid loss control treatments, production stimulation treatments, formation permeability conformance operations and treatments to reduce water production.

[0003] An example of a production stimulation treatment utilizing a high viscosity cross-linked gelled fluid is hydraulic fracturing. In hydraulic fracturing treatments, the high viscosity fluid is utilized as a fracturing fluid and also carries particulate propping agents, e.g. sand, into the fractures formed. That is, the fracturing fluid is pumped through the well bore into a formation to be stimulated at a rate and pressure such that fractures are formed and extended in the formation. Propping agent is suspended in the fracturing fluid so that it is deposited in the fractures when the gel is broken and returned to the surface. The propping agent functions to prevent the formed fractures from closing whereby conductive channels are formed through which produced fluids can flow to the well bore.

[0004] Borate ion has long been used as a cross-linking agent for forming high viscosity cross-linked gelled aqueous well treating fluids. Various sources of borate have been utilized including boric acid, borax, sodium tetraborate, slightly water soluble borates such as ulexite, and other proprietary compositions comprised of boric acid and dimers and trimers of borate ions. These solid materials which form or contain borate ion have varying solubilities in water and can cause operational problems when used as cross-linking agents in the preparation of high viscosity cross-linked gelled aqueous well treating fluids. For example, when the weather conditions are damp or wet, the solids tend to clump whereby they are difficult to meter into a gelled solution. While the solid materials are soluble in water, it is generally difficult to prepare a high concentration solution of the materials. When high concentration solutions are prepared and used, large volumes are generally required. Also, in cold weather, the high concentration solutions crystallize making pumping and motoring difficult.

[0005] Another problem involved in the preparation of a high viscosity borate ion cross-linked gelled aqueous treating fluid has been the necessity of maintaining the pH of the fluid at a high level by the addition of a caustic solution thereto. That is, the pH of the fluid controls the equilibrium between boric acid and borate ion, the borate ion being the boron species which causes gelled aqueous fluids to cross-link. When the temperature of the fluid increases, the pH of the fluid decreases. Thus, the heretofore used borate cross-linked well treating fluids have been difficult to prepare as a result of temperature and/or pH changes. By elevating the pH of the gelled fluid, the borate ion concentration in the fluid is higher. At relatively high temperatures, the pH of the treating fluid must be very high in order to allow the treating fluid to be cross-linked using a moderate amount of the borate ion source. However, when the water utilized for forming the gelled fluid contains salts such as calcium and magnesium salts which are present in brines and sea water, calcium and magnesium salts are precipitated as the pH of the fluid is raised to the high level required to minimize the quantity of borate source necessary for cross-linking. The precipitation of the salts causes even greater amounts of caustic solution to be required. The use of caustic solution to raise the pH of a borate ion cross-linked well treating fluid and the necessity of including excess borate ion in the fluid to ensure stability increases the cost of the fluid and the well treatment performed using the fluid. Thus, there is a need for improved liquid borate cross-linking compositions which can be utilized to form stable borate cross-linked gelled aqueous well treating fluids and methods of using such fluids.

[0006] The present invention provides a method of treating a subterranean zone penetrated by a well bore, which method comprises pumping into said zone a high viscosity treating fluid comprised of water, a hydrated galactomannan gelling agent and a borate cross-linking composition for buffering said treating fluid and cross-linking said hydrated galactomannan gelling agent. Said borate cross-linking composition being comprised of a low viscosity hydrocarbon liquid, an organophillic clay, a slightly water soluble borate, a buffer and a dispersing agent.

[0007] The liquid borate cross-linking compositions are basically comprised of a low viscosity hydrocarbon liquid, an organophillic clay, a slightly water soluble borate, a buffer and a dispersing agent. A particularly preferred such liquid borate cross-linking composition is comprised of diesel oil, a quaternary ammonium montmorillonite organophillic clay, urea, sodium carbonate and a dispersing agent comprised of an alkyl aromatic sulfonic acid or salt thereof.

[0008] The improved stable buffered and cross-linked gelled aqueous treating fluids of the invention are basically comprised of water, a hydrated galactomannan gelling agent and a borate cross-linking composition of this invention for buffering the treating fluid and cross-linking the hydrated galactomannan gelling agent therein. The galactomannan gelling agent is generally present in the aqueous treating fluid in an amount in the range of from about 0.1% to about 1.0% by weight of water therein. The borate cross-linking composition is generally present in the treating fluid in an amount in the range of from about 0.07% to about 1.4% by weight of water therein.

[0009] The methods of using the improved stable borate cross-linked aqueous gelled treating fluids of this invention are basically comprised of the steps of preparing such a treating fluid and then pumping the treating fluid into a subterranean zone or formation penetrated by a well bore. The fluids are more compatible with resin coated proppants by

virtue of the pH control and have been found to exhibit higher consolidation strengths when resin coated proppants are utilized than are achieved when higher pH fluids are used. The fluids also are more compatible with enzyme breakers for the gelling agent which demonstrate improved performance at lower pH.

5 [0010] The compositions of the invention contain a slightly water soluble borate. The use of such borates is described in US-A-461 9776 to which reference should be made for further details. By slightly water soluble, we mean a solubility in water at 22°C of less than 10 kg/m³.

[0011] The improved liquid borate cross-linking compositions of this invention which include a pH control additive, i. e., a buffer, and a delayed borate cross-linker, are simple and inexpensive to use in that they can be mixed and pumped at low as well as high temperatures. Further, the borate cross-linking compositions can be used to buffer and cross-
10 link aqueous well treating fluids containing hydrated galactomannan gelling agents without separately adding caustic or buffer. The use of an improved liquid cross-linking composition of this invention enables an aqueous galactomannan gelled well treating fluid to be prepared and then buffered and cross-linked by the addition of a single liquid which produces the proper pH and borate ion concentration in the treating fluid. As a result, the improved cross-linked gelled aqueous treating fluid produced is made up of fewer separate chemicals, is stable and has a predictable pumping time
15 before cross-linking takes place. Further, the treating fluid can be readily prepared using batch mixing procedures or on-the-fly procedures.

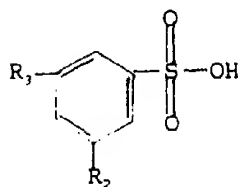
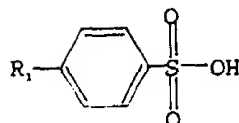
[0012] The improved liquid borate cross-linking compositions of this invention are basically comprised of a low viscosity hydrocarbon liquid, an organophillic clay, a slightly water soluble borate, a buffer and a dispersing agent. The low viscosity hydrocarbon liquid functions as a carrier for the other components of the composition and can be, for
20 example, a non-volatile hydrocarbon liquid such as hexane, heptane or octane, an aromatic compound such as benzene, toluene or xylene, mixtures of hydrocarbon compounds such as diesel oil, kerosene, mineral oil and lubricating oil, and vegetable oils such as canola, grape seed oil and the like. Of these, diesel oil is preferred. The low viscosity hydrocarbon liquid is generally included in the cross-linking compositions in an amount in the range of from about 40% to about 55% by weight of the compositions, preferably from about 45% to about 50% and most preferably about 47%.

[0013] The organophillic clay in the borate cross-linking composition functions as a suspending agent in the low viscosity hydrocarbon liquid. Examples of suitable organophillic clays are quaternary ammonium derivatized clays including, but not limited to, bentonitic clays which are treated with a quaternized amine by well known dry blending or wet slurry manufacturing processes. At least one of the radicals attached to the quaternary amine comprises a
25 member selected from the group of tallow, coco lauryl, stearyl and benzyl and the remaining radicals may be selected from the foregoing group and hydrogen, methyl and ethyl. Of these, dimethyl ditallow quaternary amine is preferred. The organophillic clay is generally included in the cross-linking compositions in an amount in the range of from about 0.5% to about 4% by weight of the compositions, preferably in an amount of from about 1.5% to about 2%.

[0014] The slightly water soluble borate included in the cross-linking compositions functions as a time delayed cross-linking agent in a galactomannan gelled aqueous well treating fluid. The slightly water soluble borates which are suitable
35 include, but are not limited to, alkaline earth metal borates, alkali metal-alkaline earth borates and mixtures thereof. Examples of such borates are probertite (NaCaB₅O₉·5H₂O), ulexite (NaCaB₅O₉·8H₂O), nobleite (CaB₆O₁₀·4H₂O), frolovite (Ca₂B₄O₈·7H₂O), colemanite (Ca₂B₆O₁₁·5H₂O), calcined colemanite (Ca₂B₆O₁₁·H₂O), priceite (Ca₄B₁₀O₁₉·7H₂O), pateronite (MgB₈O₁₃·4H₂O), hydroboracite (CaMgB₆O₁₁·6H₂O), kaliborite (Kmg₂B₁₁O₁₉·9H₂O) and other similar borates. Of the various slightly water soluble borates which can be used, colemanite, calcined colemanite, and ulexite are preferred with ulexite being the most preferred. The slightly water soluble borate used is generally included in the cross-linking compositions of this invention in an amount in the range of from about 25% to about 50% by weight
40 of the compositions, preferably in an amount of from about 35% to about 45%, and most preferably in an amount of 40%.

[0015] A variety of buffers, i.e., pH control additives can be utilized in accordance with this invention. Examples of such buffers include, but are not limited to, sodium carbonate, potassium carbonate, lithium carbonate, sodium, potassium and lithium bicarbonates and magnesium oxide. Of these, sodium carbonate is preferred. The buffer is generally included in the compositions of this invention in an amount in the range of from about 2% to about 20% by weight
45 of the compositions, preferably in an amount of from about 8% to about 12% and most preferably in an amount of about 10%.

[0016] While various dispersing agents can be used in the cross-linking compositions, a preferred dispersing agent
50 is comprised of an alkyl aromatic sulfonic acid within the scope of the formulas



or the alkaline earth metal salts thereof wherein R_1 is selected from linear alkyl groups having 8 to 24 carbon atoms and R_2 and R_3 are linear alkyl groups having from 8 to 24 carbon atoms, preferably from 12 to 14 carbon atoms.

[0017] Dispersing agents of the type described above which are preferred for use in accordance with this invention are those selected from the group of the alkaline earth metal salts of dodecylbenzene sulfonic acid with calcium dodecylbenzene sulfonate being the most preferred. The dispersing agent is generally included in the borate cross-linking compositions of this invention in an amount in the range of from about 0.2% to about 5% by weight of the compositions, preferably in an amount of from about 0.5% to about 1.5% and most preferably in an amount of about 1%.

[0018] A borate cross-linking composition of this invention is added to a galactomannan gelled aqueous well treating fluid as a single liquid component. The composition controls the pH of the treating fluid at a level whereby the delayed borate therein effectively cross-links the hydrated galactomannan gelling agent in a time period of from about 1 to about 10 minutes as determined by the vortex closure time. The vortex closure time is determined by adding 250 ml of a specified gelled fluid to a 500 ml blender jar or a Waring blender at room temperature. The speed of the blender is adjusted so that the base of the vortex created in the fluid within the jar is at the top of the retaining nut for the blade assembly, while air entrainment is minimized. The desired quantity of cross-linking composition is then added to the jar and the time for vortex closure is measured from the time of cross-linker addition.

[0019] When a shorter cross-linking time is required, a second cross-linker comprised of disodium octaborate tetrahydrate can be incorporated in the borate cross-linking composition in an amount in the range of from about 0.4% to about 2.5% by weight of the composition. The addition of the disodium octaborate tetrahydrate cross-linking agent reduces the cross-linking time to in the range of from about 5 seconds to about 3 minutes.

[0020] The vortex closure time for a 25 lb/1,000 gal gel is illustrated in the following table.

Sample No.	Delayed Cross-Linker Concentration, gal/1000 gal	Secondary Cross-Linker Concentration, gal/1000 gal	Vortex Closure Time, min:sec
1	2	0	5:49
2	2	0.1	3:09
3	2	0.2	0:54
4	2	0.4	0:14

[0021] The improved stable borate cross-linked gelled aqueous well treating fluids of this invention are basically comprised of water, a hydrated galactomannan gelling agent and a borate cross-linking composition of this invention for buffering the treating fluids and cross-linking the hydrated galactomannan gelling agents therein.

[0022] The water utilized to form the improved cross-linked well treating fluids can be fresh water, salt water, brine or any other aqueous liquid which does not adversely react with other components of the treating fluids. The water normally contains one or more salts for inhibiting the swelling of clays in the subterranean formations or zones being treated or to add weight to the treating fluid. The most common clay inhibiting salt utilized is potassium chloride, but other salts can also be used. The pH of the water is preferably in the range of from about 6 to about 8.5 to facilitate

the hydration of the galactomannan gelling agent utilized.

[0023] The galactomannan gelling agents which can be used in accordance with the present invention are the naturally occurring gums and their derivatives such as guar, locust bean, tara, honey locust, tamarind, karaya, tragacanth, carrageenan and the like. These gums are generally characterized as containing a linear back bone consisting of mannose units having various amounts of galactose units attached thereto. The gums can be manufactured to contain one or more functional groups such as cis-hydroxyl, hydroxyl, carboxyl, sulfate, sulfonate, amino or amide. Of the various galactomannan gelling agents which can be utilized, one or more gelling agents selected from the group of guar, hydroxyethylguar, hydroxypropylguar, carboxymethylguar, carboxymethylhydroxyethylguar and carboxymethylhydroxypropylguar are preferred. Of these, guar is the most preferred. When one or more of the above mentioned galactomannan gelling agents are dissolved in the water used, the gelling agents are hydrated and a viscous aqueous gel is formed. In accordance with this invention, the galactomannan gelling agent or agents utilized are dissolved in the water in an amount in the range of from 0.1% to about 1% by weight of the water, preferably in an amount of about 0.3%.

[0024] A liquid borate cross-linking composition of this invention as described above is combined with the aqueous gelled treating fluid for buffering the treating fluid and cross-linking the hydrated galactomannan gelling agent in the treating fluid. Generally the buffering and cross-linking borate composition is combined with the treating fluid in an amount in the range of from about 0.07% to about 1.4% by weight of water in the treating fluid, preferably in an amount of about 0.3%.

[0025] A particularly preferred borate cross-linking composition of this invention is comprised of diesel oil present in the composition in an amount in the range of from about 40% to about 55% by weight thereof, more preferably in an amount of from about 45% to about 50%, a quaternary ammonium montmorillonite organophillic clay present in the composition in an amount in the range of from about 0.5% to about 4% by weight thereof, more preferably in an amount of from about 1.5% to about 2%, ulexite present in the composition in an amount in the range of from about 25% to about 50% by weight thereof, more preferably in an amount of about 35% to about 45%, sodium carbonate present in the composition in an amount in the range of from about 2% to about 20% by weight thereof, more preferably in an amount of from about 8% to about 12%, and a dispersing agent comprising calcium dodecylbenzene sulfonate present in the composition in an amount in the range of from about 0.2% to about 5% by weight thereof, more preferably in an amount of from about 0.5% to about 1.5%.

[0026] The borate cross-linking compositions of this invention are stable and are easily mixed, pumped and metered at normal temperatures. The borate ion concentration in the compositions is high, and the compositions have the ability to buffer the resulting treating fluid to a pH between about 8.0 and 9.3 without the need for the addition of any other chemicals such as caustic solution. Because the pH of the treating fluid is below from about 9.3 to about 9.4, calcium and magnesium salts remain in solution.

[0027] A particularly preferred stable highly viscous borate cross-linked gelled aqueous well treating fluid of this invention is comprised of water, hydrated guar present in an amount in the range of from about 0.1% to about 1% by weight of the water, more preferably in an amount of about 0.3%, and a borate cross-linking composition of this invention for buffering the treating fluid and cross-linking the hydrated guar in the treating fluid present in an amount in the range of from about 0.07% to about 1.4% by weight of the water, more preferably in an amount of about 0.15% to about 0.35% and most preferably in an amount of 0.3%.

[0028] As will be understood by those skilled in the art a variety of conventional additives can be included in the well treating fluids such as gel stabilizers, gel breakers, clay stabilizers, bactericides, fluid loss additives and the like which do not adversely react with the treating fluids or prevent their use in a desired manner.

[0029] The improved methods of the present invention for treating a subterranean zone or formation penetrated by a well bore are basically comprised of the steps of preparing a stable high viscosity borate cross-linked gelled aqueous treating fluid of this invention and then pumping the treating fluid into the subterranean zone or formation.

[0030] While the improved treating fluids of this invention can be utilized for performing any of the various well treatments mentioned above, the treating fluids are particularly well suited for performing fracture stimulation treatments. In such treatments, a high viscosity well treating fluid is pumped through the well bore into the subterranean zone or formation to be fractured at a high rate and pressure whereby fractures are formed in the subterranean zone or formation and propping agent, such as sand, suspended in the treating fluid is carried into the fractures and deposited therein. Thereafter, the treating fluid is caused to break, i.e., revert to a thin fluid which can be reverse flowed out of the fractures leaving the proppant therein.

[0031] In order to further illustrate the compositions and methods of the present invention, the following example is given.

EXAMPLE

[0032] A fracture stimulation treatment was performed using a treating fluid of the present invention comprised of

fresh water containing 1% by weight of potassium chloride, guar gelling agent present in the treating fluid in an amount of 25 pounds per 1,000 gallons of water (0.3% by weight of water), and a liquid borate cross-linking composition of this invention for buffering the treating fluid and cross-linking the gelling agent present in an amount of 1.75 gallons per 1,000 gallons of water (0.02% by weight of water). The borate cross-linking composition was comprised of diesel oil in an amount of 47%, quaternary ammonium montmorillonite in an amount of 2%, ulexite in an amount of 40%, sodium carbonate in an amount of 10% and calcium dodecylbenzene sulfonate in an amount of 1%, all by weight of the borate cross-linking composition.

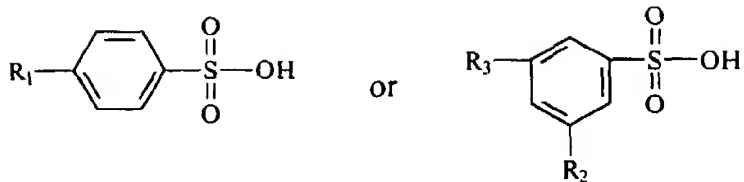
[0033] The treated formation had a temperature of 160°F and was at a depth of from 7350 feet to 7450 feet. The stimulation treatment included perforating the producing interval, acidizing the perforations and then fracturing the formation. 61,000 gallons of the above described treating fluid were pumped during the fracturing treatment and 3230 sacks (100 lbs./sack) of 20/40 ottawa sand (propping agent) were placed in the fractures at a maximum proppant concentration of 8 pounds per gallon.

[0034] The following was observed during the treatment:

1. The treating fluid was very simple to prepare as compared to prior art borate cross-linked fluids which required the use of more chemicals such as caustic and buffers.
2. The treating fluid had a higher viscosity than the prior art fluids at the same gelling agent concentration indicating less gelling agent could be used.

Claims

1. A method of treating a subterranean zone penetrated by a well bore, which method comprises pumping into said zone a high viscosity treating fluid comprised of water, a hydrated galactomannan gelling agent and a borate cross-linking composition for buffering said treating fluid and cross-linking said hydrated galactomannan gelling agent, said borate cross-linking composition being comprised of a low viscosity hydrocarbon liquid, an organophilic clay, a slightly water soluble borate, a buffer and a dispersing agent.
2. A method according to claim 1, wherein said galactomannan gelling agent is guar, hydroxyethylguar, hydroxypropylguar, carboxymethylguar, carboxylnethylhydroxyethylguar or carboxymethylhydroxypropylguar, or any mixture of two or more thereof.
3. A method according to claim 1 or 2, wherein the galactomannan gelling agent is present in the treating fluid in an amount of from 0.1% to 1% by weight of said water therein.
4. A method according to claim 1, 2 or 3, wherein said borate cross-linking composition is present in said treating fluid in an amount of from 0.07% to 1.4% by weight of said water therein.
5. A method according to any of claims 1 to 4, wherein said low viscosity hydrocarbon liquid in said borate cross-linking composition is diesel oil present in an amount of about 47% by weight of said borate cross-linking composition.
6. A method according to any of claims 1 to 5, wherein said organophilic clay in said borate cross-linking composition is dimethyl ditallow quaternary amine bentonite clay present in an amount of from 1.5% to 2% by weight of said borate cross-linking composition.
7. A method according to any of claims 1 to 6, wherein said slightly soluble borate in said borate cross-linking composition is ulexite and is present in an amount of about 40% by weight of said borate cross-linking composition.
8. A method according to any of claims 1 to 7, wherein said buffer in said borate cross-linking composition is sodium carbonate present in an amount of about 10% by weight of said borate cross-linking composition.
9. A method according to any of claims 1 to 8, wherein said dispersing agent in said borate cross-linking composition is comprised of calcium dodecylbenzene sulfonate present in said borate cross-linking composition in an amount of about 1% by weight of said borate cross-linking composition.
10. A composition according to any of claims 1 to 8, wherein said dispersing agent is comprised of an alkyl aromatic sulfonic acid of the formula



or an alkaline earth metal salt thereof, wherein R_1 is a linear alkyl group having from 8 to 24 carbon atoms and R_2 and R_3 are linear alkyl groups having from 8 to 24 carbon atoms, said agent being present in said composition in an amount of from 0.2% to 5% by weight thereof.

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(54) **Treating subterranean formations**

(57) A subterranean formation is treated with a high viscosity treating fluid comprising water, a hydrated galactomannan, a surfactant and a borate crosslinking

composition basically comprised of a low viscosity hydrocarbon liquid, an organophilic clay, a slightly water soluble borate, a buffer and a dispersing agent

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EUROPEAN SEARCH REPORT

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The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
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CATEGORY OF CITED DOCUMENTS			
<ul style="list-style-type: none"> X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background Q: non-written disclosure P: intermediate document 		<ul style="list-style-type: none"> W: theory or principle underlying the invention E: earlier patent document, but published on or after the filing date D: document cited in the application L: document cited for other reasons S: member of the same patent family, corresponding document 	

**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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20-01-2000

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CONCLUSIONS

² For more details about this annex, see Official Journal of the European Patent Office, No. 12/82.





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⑤④ **Borate crosslinked fracturing fluids.**

⑤⑦ A fracturing fluid comprises seawater, a polysaccharide polymer, a borate cross-linking agent and an alkaline agent present in a quantity sufficient to maintain the pH of the fracturing fluid above 9.5. Such a fracturing fluid has enhanced temperature stability.

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The present invention relates to fracturing fluids for fracturing of subterranean formations.

In the drilling, completion and treatment of subterranean formations penetrated by wellbores, viscous treating fluids are commonly utilized. Typically, in the art of hydraulic fracturing, a fluid is introduced through a conduit, such as tubing or casing, disposed in the wellbore into a formation sought to be fractured. The fluid is introduced at a rate and pressure sufficient to produce a fracture or fractures in the formation and extend the produced fracture or fractures from the wellbore into the formation. Upon the creation of the fracture or fractures, additional fracturing fluid containing solid proppant materials can be introduced into the fracture or fractures in the event the initial fluid did not contain any proppant. Following this treatment, the introduced fluid is recovered from the formation but the proppant remains in the produced fracture or fractures to prevent the complete closure thereof. The propped fracture creates a conductive channel extending from the wellbore into the formation.

Fracturing fluids comprised of an aqueous liquid, a hydratable polymer and a suitable cross-linking agent for cross-linking the hydratable polymer to form a polymer gel, are known. Typical aqueous liquids include water, brine or water alcohol mixtures. Typical hydratable polymers include any of the hydratable polysaccharides which are capable of gelling in the presence of a cross-linking agent to form a gel-based fluid. A known cross-linking agent is a borate cross-linking agent, which can be any convenient source of borate ions such as an alkali metal borate, an alkaline earth metal borate, an alkali metal alkaline earth metal borate or boric acid.

In order to produce borate cross-linked fluids that are stable at the high temperatures encountered in the wells, it is necessary to increase the pH of the fluid. For example, at formation temperatures of 76.7°C (170°F) or higher, it is necessary to increase the pH of the fluid to from about 9.5 to about 12.0. Often, it is convenient and even necessary to use seawater as the aqueous liquid for the fracturing fluid. However, when attempting to raise the pH of seawater to this level, the buffering action of the seawater limits the pH to approximately 9.2.

Accordingly, there is a need for a fracturing fluid containing seawater and a polysaccharide polymer cross-linked with borate which is stable at high temperatures. There is also a need for a method of producing such a fracturing fluid.

We have now devised an improved fracturing fluid and method of making such a fracturing fluid, whereby problems in the prior art are mitigated or overcome.

According to the present invention, there is provided a fracturing fluid comprising seawater (or salt water), a polysaccharide polymer, a borate cross-linking agent and an alkaline agent to provide a pH of above 9.5.

The invention also provides a method of making a fracturing fluid, which method comprises introducing a polysaccharide polymer into seawater to produce a gel, adding an alkaline agent to the gel to obtain a pH of at least 9.5, and adding to the gel a borate cross-linking agent to cross-link with the polymer, the borate cross-linking agent comprising boric acid, borax, an alkaline earth metal borate, an alkali metal alkaline earth metal borate or a mixture of two or more thereof.

By the present invention, it is possible to obtain a fracturing fluid which has enhanced temperature stability.

In order that the invention may be more fully understood, embodiments thereof will now be described, by way of example.

It is often desirable to use seawater as the aqueous liquid in a fracturing fluid comprised of an aqueous liquid, a polysaccharide polymer and a borate cross-linking agent. Borate fluids are suitable for low temperature use in the pH range of about 7.5 to about 9.0. At formation temperatures of 76.7°C (170°F) or higher, it is necessary to increase the pH to from about 9.5 to about 12.0.

Normal concentrations of an alkaline agent, such as a 25% NaOH solution, needed to raise the pH of fresh water would be in the range of 0.5 to 2.0 vol/1,000 vol of base gel fluid. However, when attempting to raise the pH of seawater to form a borate cross-linked fluid that is stable at high temperatures, the pH is generally limited to approximately 9.2 due to the consumption of the alkaline agent by ions present in the seawater. The consumption of the alkaline agent by the seawater is believed to primarily be the result of divalent ions such as Mg and Ca which are present in the seawater. These ions slowly precipitate from the solution, thereby consuming hydroxide ions and effect the pH.

The fracturing fluid of the present invention comprises an aqueous medium, a polysaccharide polymer which is capable of being cross-linked with boron, a borate crosslinking agent and an alkaline agent present in a quantity sufficient to maintain the pH of the fracturing fluid above about 9.5.

The aqueous medium of the present invention is generally seawater. The seawater contains ions such as Cl, Na, Mg and Ca and typically has a pH of around 8.0.

In order to prepare the fracturing fluid of the present invention, a hydratable polysaccharide polymer is introduced into the salt water and mixed together to form a gel. Any suitable mixing apparatus may be used for this procedure.

The hydratable polysaccharide polymer used in the present invention may be any of the polysaccharides

familiar to those in the industry which are capable of gelling to form a gel-based fluid. Suitable polysaccharides are the galactomannan gums, glucomannan gums, guar, derived guar and cellulose derivatives. Specific gelling agents are guar gum, hydroxyethyl guar, hydroxypropyl guar, carboxymethylhydroxyethyl guar, carboxymethylhydroxypropyl guar and mixtures thereof. These polysaccharides typically have molecular weights in the range of about 200,000 to about 4,000,000.

These polysaccharides have *cis*-hydroxyl groups which can complex with cross-linking agents such as titanium, zirconium, antimony, chromium and borate. For the gel of the present invention, typical polysaccharide concentrations are from about 9.07kg polymer/3.79m³ fluid (20 lb polymer/1,000 U.S. gal fluid) to about 36.29kg polymer/3.79m³ fluid (80 lb polymer/1,000 U.S. gal fluid).

After the polysaccharide polymer has been introduced into the seawater and mixed to form a gel, an alkaline agent is added to the gel to increase the fluid pH to between about 9.5 to about 12.0 in order to produce a stable borate cross-linked fluid that is stable at formation temperatures of 76.7°C (170°F) or higher. A variety of alkaline agents may be utilized to increase the fluid pH to between about 9.5 and about 12.0. Suitable alkaline agents include sodium hydroxide, potassium carbonate, sodium carbonate and potassium hydroxide.

Normal concentrations of 25% NaOH solution needed to raise the pH of fresh water are in the range of 0.5 to 2.0 vol/1,000 vol of base gel fluid. However, when attempting to raise the pH of the seawater to form a borate cross-linked fluid that is stable at high temperatures, the pH was limited to approximately 9.2 due to the buffering action of the seawater. In order to overcome the buffering action of the seawater, analytical measurements of the seawater indicated a buffer capacity equivalent to about 13 vol/1,000 vol of 25% NaOH solution, before the pH would rise about 9.2. After sufficient alkaline agent has been added to increase the pH above about 9.2, then the usual amount of 0.5 to 2.0 vol/1,000 vol of base gel fluid were predictable in controlling the pH at from about 9.5 to about 12.0 for high temperature stability.

After the alkaline agent has been added to the gel to produce a base gel having a high pH, a borate cross-linking agent is added to the gel. The concentration of cross-linking agent for efficient cross-linking was determined using viscosity as a guideline. The concentration of the cross-linking agent, is preferably in the range of from about 0.045 kg (0.1 lb) cross-linking agent, calculated as B₂O₃, per 4.54 kg (10 lb) polymer to about 0.91 kg (2.0 lb) cross-linking agent, calculated as B₂O₃, per 4.54 kg (10 lb) polymer.

This borate cross-linking agent may be any material which supplies borate ions in solution. Thus, the borate cross-linking agent can be any convenient source of borate ions. For example, the borate source may be a rapidly soluble borate source such as boric acid, borax, or Polybor, manufactured by U.S. Borax. The borate source may also be a slowly soluble borate, such as alkaline earth metal borates, alkali metal alkaline earth metal borates and mixtures thereof. Exemplary minerals which are representative of these classes of borates are as follows:

1.	Proberite:	$\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$
2.	Ulexite:	$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$
3.	Nobleite:	$\text{CaB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$
4.	Gowerite:	$\text{CaB}_6\text{O}_{10} \cdot 5\text{H}_2\text{O}$
5.	Frolovite:	$\text{Ca}_2\text{B}_4\text{O}_8 \cdot 7\text{H}_2\text{O}$
6.	Colemanite:	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$
7.	Meyerhofferite:	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$
8.	Inyoite:	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 13\text{H}_2\text{O}$
9.	Priceite:	$\text{Ca}_4\text{B}_{10}\text{O}_{19} \cdot 7\text{H}_2\text{O}$
10.	Tertschite:	$\text{Ca}_4\text{B}_{10}\text{O}_{19} \cdot 20\text{H}_2\text{O}$
11.	Ginorite:	$\text{Ca}_2\text{B}_{14}\text{O}_{23} \cdot 8\text{H}_2\text{O}$
12.	Pinnoite:	$\text{MgB}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$
13.	Paternoite:	$\text{MgB}_9\text{O}_{13} \cdot 4\text{H}_2\text{O}$
14.	Kurnakovite:	$\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$
15.	Inderite:	$\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$
16.	Preobrazhenskite:	$\text{Mg}_3\text{B}_{10}\text{O}_{18} \cdot 4\frac{1}{2}\text{H}_2\text{O}$
17.	Hydroboracite:	$\text{CaMgB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$
18.	Inderborite:	$\text{CaMgB}_6\text{O}_{11} \cdot 11\text{H}_2\text{O}$
19.	Kaliborite (Heintzite):	$\text{KMg}_2\text{B}_{11}\text{O}_{19} \cdot 9\text{H}_2\text{O}$
20.	Veatchite:	$\text{SrB}_6\text{O}_{10} \cdot 2\text{H}_2\text{O}$

The sparingly soluble borate is preferably hydrated as indicated by the minerals set forth above.

The fracturing fluids of the present invention are sensitive to the base gel concentration, borate ion concentration and pH. These fracturing fluids require precise control of pH in order to prepare these fluids to meet specific temperature conditions. For low temperature applications, namely with pH between about 8.5 to about 9.2, a buffering solution of potassium carbonate can be used to control the pH. However, for higher temperature applications, the solution of potassium carbonate would be impractical and a 25% caustic solution of NaOH is preferably used.

Various factors affect the cross-linking rate of the fracturing fluids of the present invention. These factors include the characteristics of the polymer, the solubility rate of the borate cross-linking agent, the concentration of borate, the initial pH of the fluid, and the temperature of the fluid. Borate ions were found to have a buffering effect on pH as borate ions were formed when the borate source, such as boric acid, was neutralized by the alkaline agent.

Claims

1. A fracturing fluid comprising seawater; a polysaccharide polymer; a borate cross-linking agent; and an alkaline agent to provide a pH of said fracturing fluid above 9.5.
2. A fluid according to claim 1, wherein the borate cross-linking agent comprises boric acid, borax or sodium tetraborate or a mixture of two or more thereof.
3. A fluid according to claim 1 or 2, wherein the polysaccharide polymer is guar gum, hydroxyethyl guar, hydroxypropyl guar, carboxymethylhydroxyethyl guar, carboxymethylhydroxypropyl guar or a mixture of two

or more thereof.

4. A fluid according to claim 1, 2 or 3 wherein the alkaline agent is a 25% sodium hydroxide solution.
5. A fluid according to claim 4, wherein the alkaline agent is present in a concentration of at least 13 volumes per 1000 volumes of fluid.
6. A method of preparing a fracturing fluid, which method comprises the steps of introducing a polysaccharide polymer into salt water to produce a gel; adding an alkaline agent to the gel in a quantity sufficient to obtain a pH of said gel above 9.5; and adding a borate crosslinking agent to the gel to cross-link with the polymer, the borate cross-linking agent comprising boric acid, borax, an alkaline earth metal borate, an alkali metal alkaline earth metal borate or a mixture of two or more thereof.
7. A method according to claim 6, wherein the polysaccharide polymer is guar gum, hydroxyethyl guar, hydroxypropyl guar, carboxymethylhydroxyethyl guar, carboxymethylhydroxypropyl guar or a mixture of two or more thereof.
8. A method according to claim 6 or 7, wherein the alkaline agent is a 25% sodium hydroxide solution.
9. A method according to claim 8, wherein the alkaline agent is added in an amount to provide at least 13 volumes per 1000 volumes of fluid.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 93 30 8221

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cls.)
X	CHEMICAL ABSTRACTS, vol. 102, no. 12, 25 March 1985, Columbus, Ohio, US; abstract no. 98127u, 'Drilling fluids gelled by borax-boric acid' * abstract * & HU-A-33 210 (MAGYAR SZENHIDROGENIPARI KUTATO-FEJLESZTO INTEZET) 29 October 1984	1,2,4,5	C08L5/14 E21B43/26
X	US-A-3 058 909 (L. R. KERN) * column 3, line 72 - column 4, line 6 * * column 4, line 30 - line 40 *	1-3,6,7	
A	US-A-3 146 200 (A. M. GOLDSTEIN) * column 1, line 42 - line 63 * * column 2, line 11 - line 15 * * column 3, line 46 - line 58 * * claim 1 *	1,3,6,7	
A	JOURNAL OF POLYMER SCIENCE, POLYMER PHYSICS EDITION vol. 28, no. 13, 1990, NEW YORK US pages 2445 - 2461 E. PEZRON ET AL. 'Rheology of galactomannan-borax gels' * page 2445, line 17 - line 18 * * page 2449, line 42 - line 44 * * page 2457, line 17 - line 26; figure 10 *	1-5	TECHNICAL FIELDS SEARCHED (Int.Cls.) C08L E21B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 7 January 1994	Examiner Mazet, J-F
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	

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